

Supplementary material

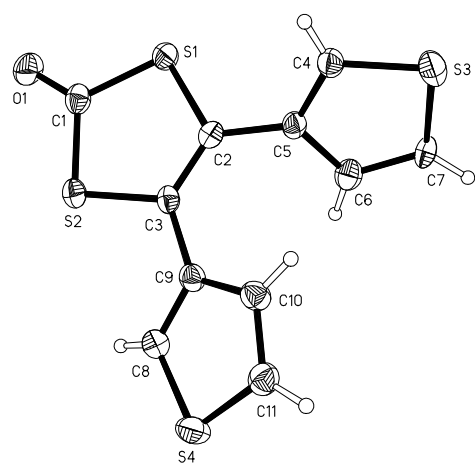
Electropolymerisation studies on a series of thiophene substituted 1,3-dithiole-2-ones: solid state preparation of a novel TTF derivatised polythiophene

Maher Kalaji, Patrick J. Murphy,* Anna K. Croft, Adam Charlton, Susan J. Roberts-Bleming, Tania Anjos,
School of Chemistry, University of Wales, Bangor, Gwynedd, LL57 2UW, UK
Email: chs027@bangor.ac.uk

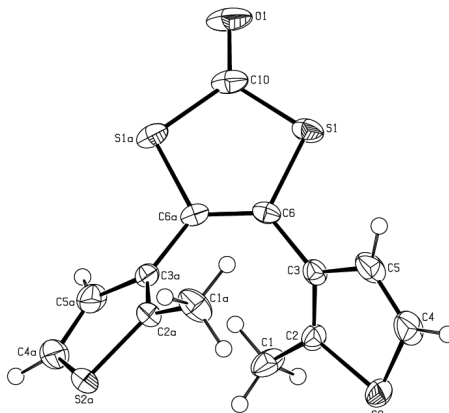
Simon J. Coles and Michael B. Hursthouse,
School of Chemistry, University of Southampton, Southampton, SO17 1BJ, UK
Email s.j.coles@soton.ac.uk

X-ray crystallography

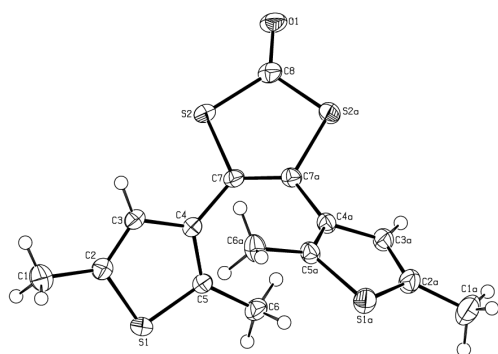
The molecular structures of **Th-3,3**, **Th-3,3(2,2'-Me)** and **Th-3,3(2,2',5.5'-Me)** are composed of a dithiolene core with two thiophene moieties in the 4 and 5 positions. In **Th-3,3** the thiophene substituents form dihedral angles of 56.47° and 25.07° (for S3, C4>C7 and S4, C8>C11 respectively) with respect to the dithiolene. The crystal structure of **Th-3,3** primarily arises from an intermolecular interaction between O1 and S3 (3.090(6)Å), forming a chain of molecules parallel to the b axis, which then pack according to requirements to optimise Van der Waals forces with an approximate separation between chains of 4.6Å. **Th-3,3(2,2'-Me)** forms an angle of 50.02° between the dithiolene and thiophene units with the second group having an identical angle due to space group symmetry. There are no classical hydrogen bonds in this structure, which packs to optimise steric and electronic considerations. **Th-3,3(2,2',5.5'-Me)** forms an angle of 46.66° between the dithiolene and thiophene units with the second angle equivalent due to a symmetry operation imposed by the space group. In the absence of any hydrogen bonds the structure packs to optimise steric and electronic considerations.



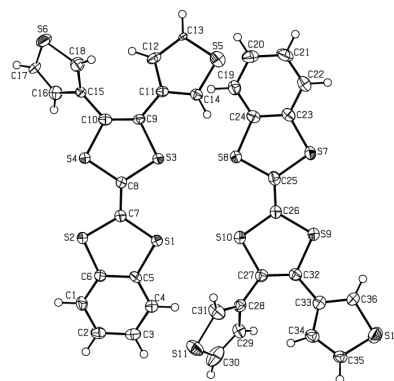
a)



b)



c)



b)

Figure 2 X-ray structures of a) Th-3,3, b) Th-3,3(2,2'-Me), c) Th-3,3(2,2',5.5'-Me) and d) 8.

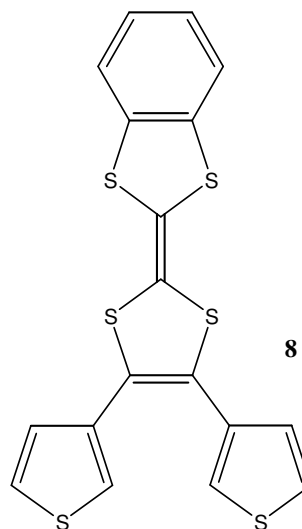
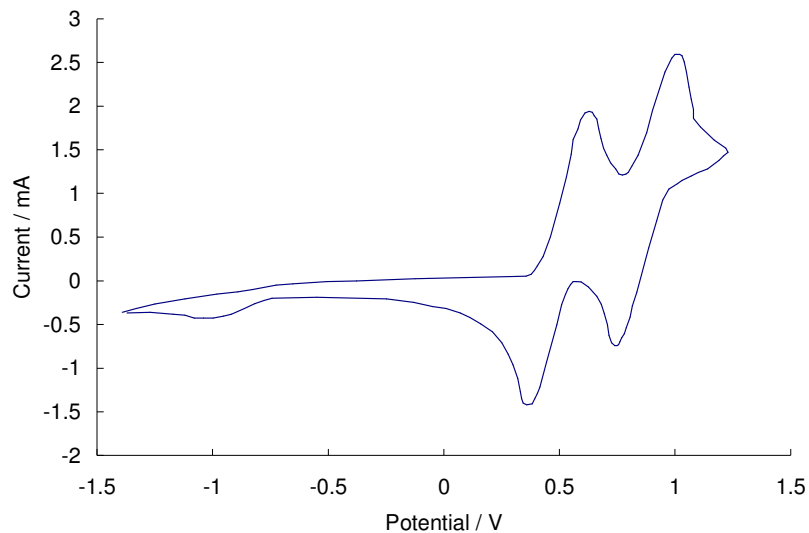
The data collection and refinement parameters of structures **Th-3,3**, **Th-3,3(2,2'-Me)**, **Th-3,3(2,2',5.5'-Me)** and **8** are presented in Table 2. X-ray diffraction data were collected on a Bruker-Nonius KappaCCD area detector situated at the window of a rotating anode [$\lambda(\text{Mo-}K\alpha) = 0.71073\text{\AA}$]. The structures were solved by direct methods and refined using programs of the SHELXL family.¹ Hydrogen atoms were included in the refinement, but their displacement parameters and positions were constrained to ride on the atoms to which they are bonded. The methyl group in **Th-3,3(2,2'-Me)** exhibits rotational disorder and the position of the hydrogen atoms are refined over two separate sites of 55% and 45% occupancy. Both the thiophene groups in compound **8** are subject to rotational disorder, such that a S atom and an aromatic C atom occupy the same site (in a 58:42 and 65:35 ratio for the groups containing S6 and S11 respectively). The data were corrected for absorption effects using SORTAV.² The complete crystallographic data have also been deposited with the Cambridge Crystallographic Data Centre [Deposition numbers are CCDC703474, CCDC703475, CCDC216340 and CCDC216250 for compounds **Th-3,3**, **Th-3,3(2,2'-Me)**, **Th-3,3(2,2',5.5'-Me)** and **8** respectively].

	Th-3,3	Th-3,3(2,2'-Me)	Th-3,3(2,2',5.5'-Me)	8
Empirical formula	C ₁₁ H ₆ OS ₄	C ₁₃ H ₁₀ OS ₄	C ₁₅ H ₁₄ OS ₄	C ₁₈ H ₁₀ OS ₆
Formula weight	282.40	310.45	338.50	418.68
Crystal system	Monoclinic	Orthorhombic	Monoclinic	Triclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> bcn	<i>C</i> 2/ <i>c</i>	<i>P</i> -1
<i>a</i> / \AA	9.3195(4)	14.5002(3)	15.2123(4)	9.300(2)
<i>b</i> / \AA	15.3964(11)	13.4816(3)	14.4906(3)	12.701(3)
<i>c</i> / \AA	7.920(3)	7.0091(2)	9.0328(2)	16.235(3)
α / $^\circ$	90.0	90.0	90.0	80.75(3)
β / $^\circ$	96.040(3)	90.0	125.860(2)	85.77(3)
γ / $^\circ$	90.0	90.0	90.0	68.59(3)
<i>V</i> / \AA^3	1130.1(4)	1370.18(5)	1613.72(6)	1761.9(7)
<i>Z</i>	4	4	4	4
μ /mm ⁻¹	0.811	0.676	0.580	0.773
<i>T</i> /K	150	150	150	150
Crystal size /mm	0.2 × 0.1 × 0.1	0.2 × 0.2 × 0.15	0.3 × 0.3 × 0.2	0.25 × 0.25 × 0.05
θ_{max} (°)	25.98	25.99	25.03	26.34
Reflections collected	6137	5309	9039	28931
Independent reflections	2194	1343	1433	7067
<i>R</i> _{int}	0.0425	0.0298	0.0356	0.0985
Refined parameters	164	93	121	461
<i>R</i> (<i>F</i> , <i>F</i> ² > 2 σ)	0.0393	0.0380	0.0289	0.0522
<i>R</i> _w (<i>F</i> ² , all data)	0.0960	0.1049	0.0749	0.1334
Goodness of fit (<i>F</i> ²)	0.975	1.081	1.051	0.977
Difference map extremes /e \AA^{-3}	0.389, -0.352	0.672, -0.600	0.251, -0.247	0.692, -0.569

Table 2. Selected data collection and refinement parameters for **Th-3,3**, **Th-3,3(2,2'-Me)**, **Th-3,3(2,2',5.5'-Me)** and **8**.

CV data for compound **8**

Compound **8** was analysed by cyclic voltammetry in a 0.1 M solution of TBATFB/MeCN showing a behaviour typical of TTF derivatives in which the characteristic TTF redox couples appeared at $E_{\text{ox}}^1 + 0.68$ V and $E_{\text{ox}}^2 + 1.07$ V vs. Ag wire. These values are shifted towards more positive potentials compared to TTF.



References

- 1 G. M. Sheldrick, *Acta. Crystallogr. Sect. A*, **64**, (2008), 112.
- 2 R. H. Blessing, *J. Appl. Cryst.* **30**, (1997), 421.